SUSTAINABLE ENERGY STORAGE – WITH HOT AIR, OR COLD AIR OR LIQUID AIR

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Abstract. In memory of Sir David John Cameron MacKay FRS FInstP FICE (22 April 1967 - 14 April 2016). David was passionate about sustainable energy. One key element for sustainable energy is energy storage. As a small tribute, this article presents a review from a physics perspective of the thermodynamics of compressed air energy storage. Firstly, I treat adiabatic compressed air energy storage, where the heat of compression of the air is kept in the compressed air. Then I discuss improvements that can be made by combining compressed air energy storage with external heat stores. Next, I address isothermal compressed air energy storage, where the temperature is allowed to equilibrate with the environment. In each case, I consider two scenarios: underground caverns and underwater airbags. Finally, I address the case where the air is compressed and cooled so much that it liquifies. Throughout, I explain that the real point is to store available work, called exergy in the engineering community, rather than energy. Although my treatment is mostly from the ideal point of view of quasistatic processes, I give some pointers to technological implementations of the various methods and to some references on their thermodynamic efficiencies.

1. Introduction

My brother David made a huge public impact with his talks and book on "Sustainable energy – without the hot air" [1]. The subtitle reflected his straight-talking manner, which was highly beneficial to the debate on sustainable energy and influential in his role as Chief Scientific Adviser to the UK Department of Energy and Climate Change (2009-2014).

Yet there *is* a contribution to sustainable energy to be made by hot air – in the physical sense – namely to energy storage.

As David pointed out in Chapter 26 of [1], the transition from fossil fuels towards renewable energy sources is workable only if practical methods for storing large amounts of energy, or deferring consumption, are developed. This is because the sun shines during only daytime, wind is highly variable, and the times we want energy are also variable. Fossil fuels are a great way of storing energy with relatively high energy density, extremely long durability and easy release of the energy in useful forms such as electricity, heat and locomotion, but our ability to put the process into reverse is limited. Although we are able to imitate the creation of fossil fuels with biofuels, they have environmental and social drawbacks; similarly we can synthesise methane from water, CO_2 and electricity, but the process is currently not competitive. If we can not

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or will not defer (or bring forward) sufficient consumption, we need to be able to store excess wind or solar energy and use it later.

One successful way to store electrical energy is pumped hydroelectric storage, where excess electricity is used to pump water from a low to a high reservoir and the water flowing back down generates electricity when required, but there are geographical limits to where such schemes can be built.

Much activity is devoted to battery storage but at least at present it is very expensive per unit of capacity and its highest potential is for balancing on timescales of at most an hour (capacity divided by maximum charge or discharge rate) whereas the biggest need is for timescales of a day or a week. At another extreme, there is much excitement about hydrogen storage, but it is also very expensive at present and is best adapted to catering for timescales of a week to a year.

An alternative way to store energy is to compress air. This appears to be the most promising method for timescales of two days to two weeks [2]. In the process, the air tends to become hot, hence the first part of my subtitle. David took a great interest in energy storage ideas, including compressed air (even if the only place I found it in his book is for regenerative braking in cars). Indeed he served on the External Advisory Board for an EPSRC-supported project on Integrated Market-fit Affordable Grid-scale Energy Storage (IMAGES), one of whose principal technologies was compressed air, and on which I was an investigator.

One might think that the scope for compressed-air energy storage is very limited, because it would require large volumes, high pressures and good sealing, to store much energy, but for example there are underground salt deposits in many parts of the world, which can be excavated by solution-mining to form large self-sealing caverns into which air can be compressed to 150 bar (about 15 MPa) or more.

There are two compressed-air energy-storage facilities in commercial operation: Huntorf in Germany, and McIntosh, Alabama in the USA. Both store the compressed air in salt caverns. They have the design defect, however, that much of the heat of compression is wasted by purposely cooling the air to keep its temperature within safe bounds for the cavern and to increase the amount of air that can be compressed into the cavern for given pressure limit. This would not in itself be a problem if done reversibly, but when the air is released to provide electricity it is re-heated by burning gas, rather than recovering the heat from the environment. Thus they are highly inefficient (Huntorf's efficiency is 24% according to Jasmin Lückert [3], though others put it at 42% [4] and to be fair one should make a comparison with the efficiency of converting gas to electricity).

The plan of various groups around the world, including our IMAGES project, is to develop compressed-air energy-storage technology in which the heat of compression is also stored and reused for the expansion phase. In principle, such a scheme could approach 100% efficiency.

In this article, I review the thermodynamics of compressed-air energy storage (CAES). Thermodynamics is a difficult topic for many people, including myself, and I am still looking for a good presentation (see my book review [5] for some comments). One issue is that it depends on the concept of entropy, which is not as tangible as pressure and temperature (but see [6] for a good presentation). Another is that it is not energy per se that we want to store, but "available energy", which engineers call "exergy". This

is the maximum amount of work that can be extracted from a system by returning it to normal temperature and pressure. The existence of a maximum is a consequence of the second law of thermodynamics. For a system like a gas the exergy is given by $W = U + P_0V - T_0S - A_0$, where U is the internal energy, V is volume, S is entropy, P_0 and T_0 are the ambient pressure and temperature (on absolute scale) and A_0 is a constant to make $W = 0$ at ambient conditions.

Exergy gets scant mention in most physics textbooks on thermodynamics. For example, in the classic text by Callen [7], it comes only in an exercise (4.5-20) and under the name "availability", though engineers make a distinction between the two terms [8]. Exergy is distinct from the Helmholtz and Gibbs free energies, because the free energies apply to conditions of constant temperature and either volume or pressure respectively, whereas exergy allows for changes in all of these.

Thermodynamics is one of the many topics on which my brother and I conversed. Indeed we were intrigued by how biomotors such as myosin (the principal biomolecule in muscle) convert chemical energy to work, and this led to a joint paper [9] in which we proposed a mechanism whereby the phosphate ion produced by hydrolysis of ATP (adenosine triphosphate) enlarges the volume of the binding pocket by a big factor until an opening is created at a location with opposite charge, the enlarging of the pocket driving the conformation change of myosin (it is a type of Szilard engine). In that context, the biomolecules are strongly thermally coupled to their environment, so one might worry that exchange of heat would make the process inefficient, but isothermal processes can be close to 100% efficient if operated slowly ("quasistatically") and close to thermal equilibrium, just as adiabatic ones can ("adiabatic" means quasistatic with no heat flow to the surroundings).

The latter point introduces an alternative for compressed-air energy storage, namely to store and release it at thermal equilibrium with the environment, hence the second part of my subtitle, "cold air". This could be appropriate for under-sea compressed-air storage schemes where a polymer bag pinned to the ocean floor is inflated with air. The idea is being promoted to accompany offshore wind farms in order to reduce the variability of their power output. To achieve high energy density the floor would need to be deeper than for the offshore wind farms in the North Sea or the bag could be replaced by an underwater cavern excavated from the rock deep under the sea floor with a second pipe for the air to displace water. It might be hard, however, to keep the heat of compression in the air in a plastic bag surrounded by cold water, or in a cavern with an air-water interface, so it could be a good idea to encourage thermal equilibration to ensure close to isothermal operation and thereby exploit a second regime of high efficiency. On release, assuming thermal equilibration in the process, the ocean returns the missing heat.

Another possibility is to compress and cool the air so much that it liquifies, as in the third part of my subtitle. This has the advantage that the resulting liquid air takes up much less space than gaseous air, so it could be stored in above-ground tanks rather than having to excavate an underground cavern, for equal energy storage capacity.

I will treat all three cases: hot air, cold air and liquid air.

For an old review of the thermodynamics of CAES see [10], and for a recent survey see [11]. Several recent overviews can be found on the web too. Much more can be found

in [4]. For an overview of current technologies, see [12]. Finally, the IMAGES project ran a day on the "Future of CAES in the UK" on 12 September 2016, from which some presentations are available [3].

2. CAES with hot air

I will begin with some fairly basic material to make sure everyone is on board. Expert readers can skip to the first subsection.

Let us treat air as an ideal gas. This is a reasonable approximation if we neglect moisture in the air and do not approach liquefaction. Then

$$PV = nRT, \tag{1}$$

where P is the pressure, V the volume, n the number of moles, $R \approx 8.314 JK^{-1}mol^{-1}$ the gas constant, and T the (absolute) temperature.

The internal energy of air is close to $U = \frac{5}{2}nRT$. This is because it consists mainly of diatomic molecules (N_2, O_2), for which at the relevant range of temperatures the internal energy is in three dimensions of translation and two dimensions of rotation (about axes perpendicular to the axis of the molecule). The energy in each of these is on average $\frac{1}{2}k_BT$, where k_B is Boltzmann's constant (converting units from temperature to energy), making $\frac{5}{2}k_BT$ per molecule and hence $\frac{5}{2}RT$ per mole ($R = N_Ak_B$, where N_A is the Loschmidt-Avogadro number of molecules in a mole).

To understand the storage of energy by compressed air, we will need not only its internal energy but also its entropy. From a microscopic view, the entropy of a body is the logarithm of the available volume for its configurations and momenta, or for its wavefunction. But it can be defined from a purely macroscopic view based on axioms suggested by experiments in the 1800s (for a more recent axiomatic approach, see [13]). These lead to the existence of an entropy function S and absolute temperature T for a body in thermal equilibrium, such that in a quasistatic injection of heat δQ without doing any work, the entropy increases by $\delta S = \frac{\delta Q}{T}$, and to the vital second law of thermodynamics, that the total entropy of an isolated collection of systems can not decrease.

In the process of injecting heat, the body becomes hotter (there are systems with negative specific heat, like stars, but the axioms do not apply there, because of the long range of the gravitational interaction). For quasistatic injection of heat at rate $\dot{Q}(t)$ as a function of time t, so that the body has a uniform temperature $T(t)$ at time t, the increase in entropy from time t_0 to t_1 is

$$\Delta S = \int_{t_0}^{t_1} \frac{\dot{Q}(t)}{T(t)}\, dt.$$

In particular, for a body with thermal capacity $C(T)$ per degree,

$$\Delta S = \int_{T_0}^{T_1} \frac{C(T)}{T}\, dT, \tag{2}$$

for a change from temperature T_0 to T_1.

Now for an ideal gas with $U = \frac{5}{2}nRT$, if we keep it at constant volume and put in heat we deduce that its thermal capacity per degree is $C_v = \frac{5}{2}nR$. Thus by integrating (2), the entropy increase is $\Delta S = \frac{5}{2}nR \log \frac{T_1}{T_0}$.

If on the other hand we compress it quasistatically from volume V_0 to V_1 so that it has a well-defined pressure P at each time, then we have to do work $W = -\int_{V_0}^{V_1} P\, dV$. If we allow heat to flow out to keep its temperature T constant and use (1) then

$$W = -\int_{V_0}^{V_1} \frac{nRT}{V}\, dV = nRT \log \frac{V_0}{V_1}.$$

Being at constant temperature and an ideal gas, its internal energy does not change so this work must come out as heat. So the heat flowing out is $nRT \log \frac{V_0}{V_1}$ and the entropy decreases by $nR \log \frac{V_0}{V_1}$.

Combining the results of the previous two paragraphs, we deduce that the entropy increase for a general change of state of our ideal gas is

$$\Delta S = nR \left(\tfrac{5}{2} \log \frac{T_1}{T_0} - \log \frac{V_0}{V_1} \right).$$

To cater for situations where the number of moles changes it is convenient to consider the volume per mole V/n. Thus the entropy of n moles of air is

$$S = nR \left(\log \frac{VT^{\frac{5}{2}}}{n} + cst \right), \tag{3}$$

where the constant provides an arbitrary reference value of entropy per mole.

If the air is compressed or expanded quasistatically with no heat transfer ("adiabatic") then its entropy is conserved, so

$$VT^{\frac{5}{2}} = constant. \tag{4}$$

Using (1) one obtains the more familiar form

$$PV^{\frac{7}{5}} = constant.$$

Think of one mole of air starting at "normal" temperature $T_0 = 293.15K$ and pressure $P_0 = 101325Pa$. Then $RT_0 \approx 2437J$ and the air occupies volume $V_0 = RT_0/P_0 \approx 0.024055m^3 = 24.055l$. If it is compressed by a factor α to volume V_0/α then its pressure is raised by a factor $\alpha^{\frac{7}{5}}$ and its temperature by a factor $\alpha^{\frac{2}{5}}$.

We will treat two types of adiabatic store: an insulated cavern and an insulated underwater airbag.

2.1. **Insulated cavern.** Suppose an insulated cavern of volume V_c. At normal temperature T_0 and pressure P_0 it would contain $n_0 = P_0V_c/RT_0$ moles of air. If we increase this to n moles by adiabatic compression of atmospheric air into the cavern, then $T = T_0(\frac{n}{n_0})^{\frac{2}{5}}$, $P = P_0(\frac{n}{n_0})^{\frac{7}{5}}$, and the work we have to do is the increase in internal energy of the air minus the work done by atmospheric pressure (neglecting the change

in gravitational potential energy of the air):

$$W = \tfrac{5}{2} nRT_0 \left(\left(\frac{n}{n_0} \right)^{\frac{2}{5}} - 1 \right) - (n - n_0) RT_0. \tag{5}$$

To distinguish it from the stored internal energy, engineers refer to W as the stored "exergy". Exergy is defined as the maximum amount of work that could be extracted by letting a system relax back to atmospheric temperature and pressure. Letting $W_0 = n_0 RT_0 = P_0 V_c$, equation (5) can be written as

$$\frac{W}{W_0} = \tfrac{5}{2} \left(\frac{n}{n_0} \right)^{\frac{7}{5}} - \tfrac{7}{2} \frac{n}{n_0} + 1.$$

The dependence of W, T and P on n is shown in Figure 1. In particular, the stored exergy is a convex function of the number of moles of air stored. Note that exergy can also be stored by removing air from the cavern ($n < n_0$).

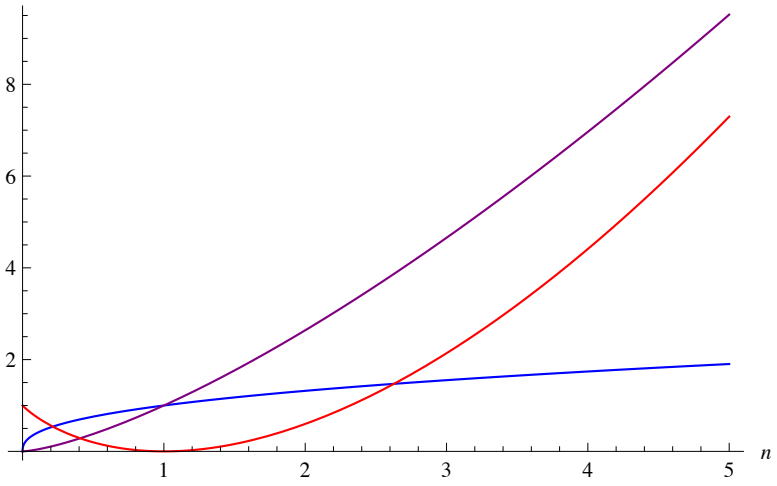

FIGURE 1. The stored exergy W (red), temperature T (blue) and pressure P (purple) in an insulated cavern as a function of the number n of moles stored. The units are $P_0 V_c$, T_0, P_0 and n_0.

If P_{max} is the maximum pressure the cavern can sustain then the maximum exergy it can store (using pressures above atmospheric) is

$$W_{max} = P_0 V_c \left(\tfrac{5}{2} \frac{P_{max}}{P_0} - \tfrac{7}{2} \left(\frac{P_{max}}{P_0} \right)^{\frac{5}{7}} + 1 \right). \tag{6}$$

2.2. **Insulated underwater airbag.** Alternatively, suppose an insulated airbag at depth h under water of density ρ. We neglect the strain energy in the bag and the height of the bag compared to the depth h of water. Then air in the bag is at constant pressure P_b with $P_b - P_0 = \rho g h$ (g being the acceleration due to gravity). For a more refined treatment, see [14]. If we pump n moles of air from the atmosphere into the bag quasistatically without loss of heat then the temperature in the airbag becomes

$T_b = T_0(\frac{P_b}{P_0})^{\frac{2}{7}}$. The volume V to which the air expands the airbag is $V_0(\frac{P_b}{P_0})^{-\frac{5}{7}}$, where $V_0 = nRT_0/P_0$ is the volume of the air at normal temperature and pressure. The work W we have to do is the increase in internal energy of the air plus the increase in potential energy of the water displaced from depth h to the surface, minus the nett work done by the atmosphere (it does some work on the gas but then has some work done on it by the displaced water; neglect the change in gravitational potential energy of the air again). There are some cancellations and the final result is

$$W = \tfrac{7}{2}nRT_0\left(\left(\frac{P_b}{P_0}\right)^{\frac{2}{7}} - 1\right).$$

Thus the stored exergy is proportional to the number of moles stored: $W = wRT_0n$, with

$$w = \tfrac{7}{2}\left(\left(\frac{P_b}{P_0}\right)^{\frac{2}{7}} - 1\right). \tag{7}$$

The constant of proportionality w, temperature T_b and volume V as functions of the pressure ratio are shown in Figure 2.

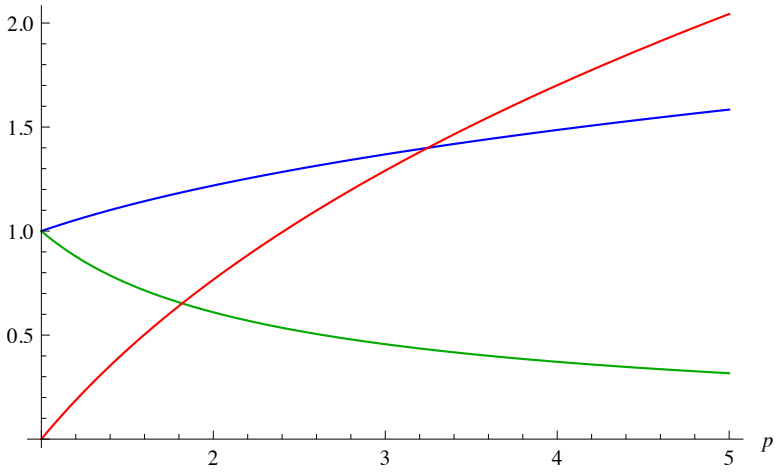

FIGURE 2. The stored exergy coefficient w (red), temperature T_b (blue) and volume V (green), relative to atmospheric conditions, for an insulated airbag under water, as functions of the pressure ratio $p = \frac{P_b}{P_0}$.

If the airbag has a maximum volume of V_{max} then the maximum exergy it can store at pressure P_b is

$$W_{max} = \tfrac{7}{2}P_0V_{max}\left(\frac{P_b}{P_0} - \left(\frac{P_b}{P_0}\right)^{\frac{5}{7}}\right). \tag{8}$$

3. CAES WITH HEAT STORES

Caverns are limited in the temperatures and pressures they can withstand. Thus to increase the exergy storage by a given cavern one could build an associated heat store

and store some of the heat of compression in it, thereby allowing one to put more air into the cavern. If the heat exchange is carried out with negligible temperature difference between the air and the store at all stages then little entropy increase occurs for the combined system and the work put in can be recovered with nearly 100% efficiency.

Similarly, airbags are limited in the temperatures they can withstand, and insulating an airbag underwater sufficiently well might be difficult if there is a large temperature difference. So it could be good to store some of the heat separately.

Thus we consider coupling a cavern or an airbag to a heat store. We characterise the heat store by a thermal capacity $C(T)$ per degree at temperature T. The simplest case is a constant thermal capacity C_0 per degree, but we can allow for variable thermal capacity. In particular we can allow for phase-change heat stores, in which $C(T)$ has essentially a delta-function at the phase-change temperature, corresponding to the latent heat for the phase change. We begin with an airbag, because the analysis is easier.

3.1. **Insulated underwater airbag with heat store.** Let us suppose we couple an insulated underwater airbag to a heat store. Then the entropy increase ΔS in pumping n moles of air into the bag, starting from empty and allowing the temperatures in the airbag and heat store to equilibrate to a temperature T, is

$$\Delta S = nR \log \left(\left(\frac{T}{T_0} \right)^{\frac{7}{2}} \frac{P_0}{P_b} \right) + \int_{T_0}^{T} \frac{C(t)}{t}\, dt. \tag{9}$$

If the compression is done without change in entropy (i.e. there is never a difference in temperature between the bag and the store) then we deduce that the temperature T is related to the number n of moles by

$$nR = \frac{\int_{T_0}^{T} \frac{C(t)}{t}\, dt}{\log \frac{P_b}{P_0} - \frac{7}{2} \log \frac{T}{T_0}}. \tag{10}$$

If the heat store has constant thermal capacity C_0 per degree, this reduces to

$$n = \frac{C_0}{R} \frac{\log \frac{T}{T_0}}{\log \frac{P_b}{P_0} - \frac{7}{2} \log \frac{T}{T_0}},$$

which implies

$$\log \frac{T}{T_0} = \frac{nR \log \frac{P_b}{P_0}}{C_0 + \frac{7}{2} nR},$$

equivalently

$$\frac{T}{T_0} = \left(\frac{P_b}{P_0} \right)^{\frac{1}{\frac{7}{2} + \frac{C_0}{nR}}}. \tag{11}$$

In general, the work done is

$$W = \tfrac{7}{2} nR(T - T_0) + \int_{T_0}^{T} C(t)\, dt, \tag{12}$$

and this is the exergy stored. Substituting the expression (10) into (12), we can write

$$W = \frac{(T-T_0)\int_{T_0}^{T}\frac{C(t)}{t}\,dt}{\frac{2}{7}\log\frac{P_b}{P_0}-\log\frac{T}{T_0}} + \int_{T_0}^{T} C(t)\,dt.$$

In the case of constant thermal capacity C_0 per degree, this reduces to

$$W = \frac{C_0(T-T_0)\log\frac{P_b}{P_0}}{\log\frac{P_b}{P_0}-\frac{7}{2}\log\frac{T}{T_0}},$$

which can be written in terms of n as

$$W = \left(\exp\left(\frac{nR\log\frac{P_b}{P_0}}{C_0+\frac{7}{2}nR}\right)-1\right)(C_0+\tfrac{7}{2}nR)T_0.$$

Writing $\tilde{n} = \frac{nR}{C_0}$ reduces the formula to

$$W = C_0T_0(1+\tfrac{7}{2}\tilde{n})\left(\left(\frac{P_b}{P_0}\right)^{\frac{\tilde{n}}{1+\frac{7}{2}\tilde{n}}}-1\right). \tag{13}$$

We can also calculate the volume in the airbag from (1):

$$V = \frac{\tilde{n}C_0T_0}{P_b}\left(\frac{P_b}{P_0}\right)^{\frac{\tilde{n}}{1+\frac{7}{2}\tilde{n}}}. \tag{14}$$

The results are illustrated in Figure 3. We see it makes the dependence of W on n nonlinear (for $C_0 \neq 0$) but the asymptotic slope for large n is still w of (7).

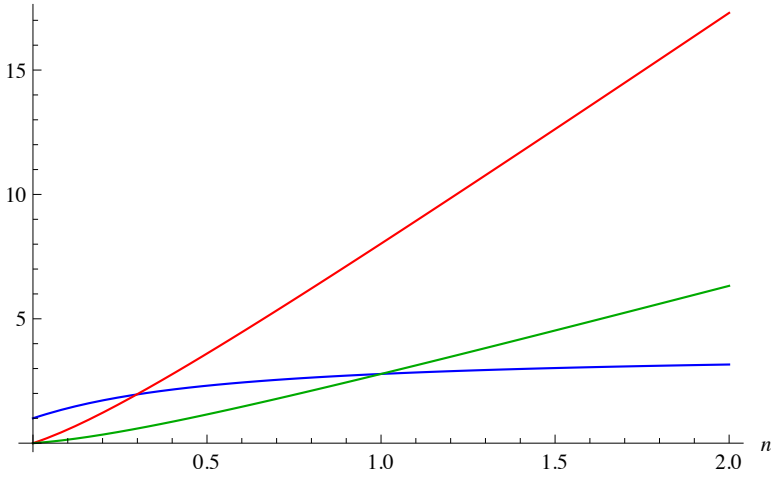

FIGURE 3. Temperature T (blue), volume V (green) and stored exergy W (red) against number n of moles of stored air for an insulated airbag with heat store, taking $P_b/P_0 = 100$. The units are T_0, C_0T_0/P_b, C_0T_0 and $\frac{C_0}{R}$ respectively.

If the airbag has a maximum volume V_{max} then combined with the heat store the maximum exergy they can store is given by eliminating n between (13) and (14). The

exergy stored as a function of pressure and volume in the airbag is plotted in Figure 4. The slope for W against V for given P and large V is asymptotically the same as the case (8) without heat store.

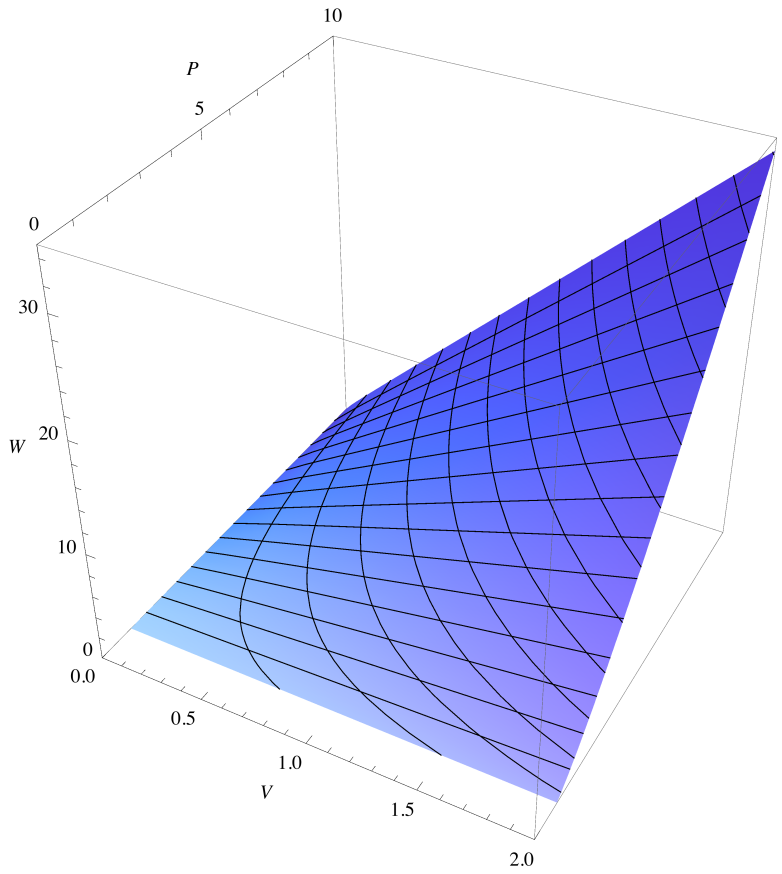

FIGURE 4. The exergy W stored as a function of bag volume V and pressure P, for insulated underwater airbag with a heat store of thermal capacity C_0 per degree. The units are C_0T_0, C_0T_0/P_0 and P_0 respectively.

3.2. **Insulated cavern with heat store.** Next we couple a cavern to a heat store. Then the entropy increase ΔS on increasing the number of moles of air in the cavern from $n_0 = P_0V_c/RT_0$ to n is

$$\Delta S = nR \log \left(\frac{n_0}{n} \left(\frac{T}{T_0} \right)^{\frac{5}{2}} \right) + \int_{T_0}^{T} \frac{C(t)}{t}\, dt. \tag{15}$$

If the change is done reversibly then this is zero and so defines a relation between n and T. In the case of a heat store with constant thermal capacity C_0 per degree, it can be solved to yield

$$\frac{T}{T_0} = \exp \frac{nR \log \frac{n}{n_0}}{\frac{5}{2}nR + C_0} = \left(\frac{n}{n_0} \right)^{\frac{1}{\frac{5}{2} + \frac{C_0}{nR}}}.$$

In general, the work done is

$$W = \tfrac{5}{2}nR(T - T_0) - (n - n_0)RT_0 + \int_{T_0}^{T} C(t)\ dt.$$

In the case of constant thermal capacity per degree, this boils down to

$$W = (\tfrac{5}{2}nR + C_0)T_0 \left(\frac{n}{n_0}\right)^{\frac{1}{\frac{5}{2}+\frac{C_0}{nR}}} - \tfrac{7}{2}nRT_0 + (n_0R - C_0)T_0. \tag{16}$$

There are now two relevant scales for n, namely n_0 and C_0/R. We can also work out the pressure from (1), namely

$$P = P_0 \left(\frac{n}{n_0}\right)^{1+\frac{1}{\frac{5}{2}+\frac{C_0}{nR}}}. \tag{17}$$

The results are plotted in Figure 5 for the case of $C_0 = nR$.

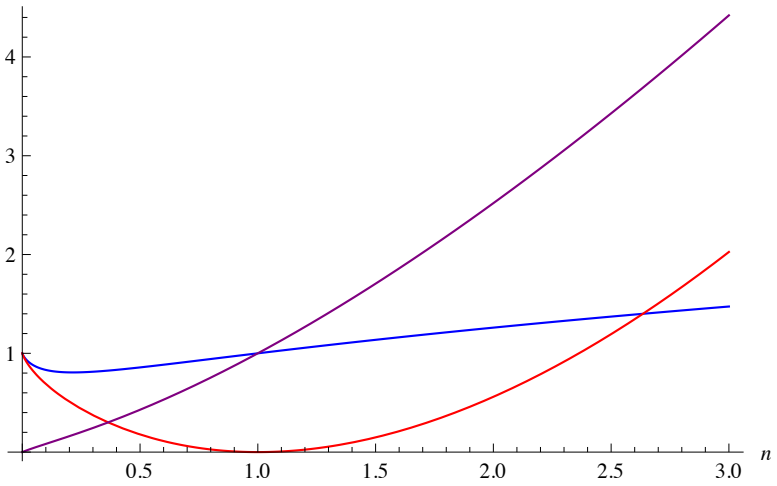

FIGURE 5. Temperature T (blue), pressure P (purple) and stored exergy W (red) as functions of the number n of moles of air in a cavern coupled to a heat store with $C_0 = n_0R$. Units are T_0, P_0, C_0T_0 and n_0, respectively.

The maximum exergy stored by the cavern plus heat store for given maximum pressure and thermal capacity per degree can be obtained by eliminating n between equations (16) and (17). It is shown in Figure 6.

3.3. **Heat stores for restricted temperature ranges.** Some CAES proposals have several heat stores, which are connected for different temperature ranges and disconnected outside those ranges. This situation can be incorporated into the above formulation by taking $C(T)$ to be the sum of the thermal capacities per degree of the heat stores that are coupled to the compressed air at temperature T.

More significantly, the compression or expansion may be carried out in more than one stage, with different heat stores in between the stages. This requires modified analysis.

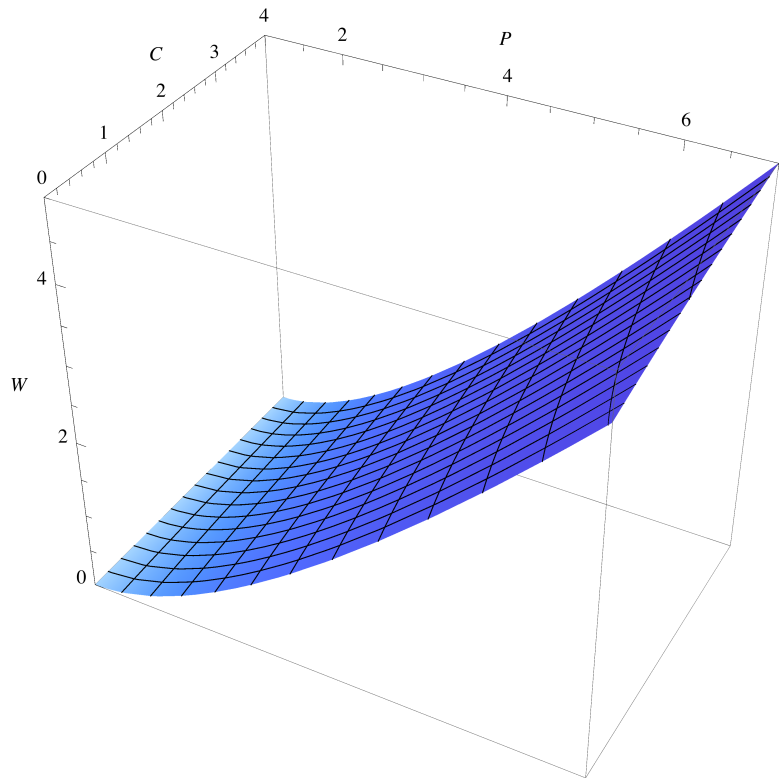

FIGURE 6. The stored exergy W for an insulated cavern with heat store, as a function of pressure P and the thermal capacity C per degree of the heat store (taken constant). Units are C_0T_0, P_0 and n_0R respectively.

Consider the case of an underwater airbag. Suppose there is a heat store between two compressor/expanders. Suppose that it operates reversibly and the heat it takes out per mole of air passing from the atmosphere to the bag is describable by some function $q(T_s)$, where T_s is the temperature of the store (one could allow it to depend on the temperature T_b in the bag too). Suppose the heat store has thermal capacity $C(T_s)$ per degree. Then on passing an infinitesimal amount dn of air from the atmosphere to the bag, the change in the temperature of the heat store is given by

$$C(T_s)dT_s = q(T_s)dn$$

This gives us

$$\frac{dT_s}{dn} = \frac{q(T_s)}{C(T_s)}. \tag{18}$$

Next, the entropy increase for the system on passing dn of air from the atmosphere to the bag is

$$dS = \left(R\left(\tfrac{7}{2}\log\frac{T_b}{T_0} - \log\frac{P_b}{P_0}\right) + \frac{q(T_s)}{T_s}\right)dn + \tfrac{7}{2}nR\frac{dT_b}{T_b}, \tag{19}$$

where T_b is the temperature in the bag. Setting dS to zero gives us

$$\frac{dT_b}{dn} = \frac{T_b}{n}\left(\tfrac{2}{7}\log\frac{P_b}{P_0} - \log\frac{T_b}{T_0} - \frac{2q(T_s)}{7RT_s}\right). \tag{20}$$

Finally the work done to pass dn is

$$dW = \tfrac{7}{2}R(T_b - T_0)dn + \tfrac{7}{2}nRdT_b + C(T_s)dT_s.$$

Combining these we obtain

$$\frac{dW}{dn} = R\left(\tfrac{7}{2}(T_b - T_0 - T_b\log\frac{T_b}{T_0}) + T_b\log\frac{P_b}{P_0}\right) - \left(\frac{T_b}{T_s} - 1\right)q(T_s). \tag{21}$$

Integrating these three differential equations (18, 20, 21) with respect to n yields the trajectory of the system. I don't know a realistic model for the function q. It depends on the design of the compressor/expanders. But in principle I believe this is the way to treat ideal intermediate heat stores.

One can treat the case of intermediate heat stores for a cavern similarly. Denote the cavern temperature by T_c. Then

$$dS = \left(R\left(\tfrac{5}{2}\log\frac{T_c}{T_0} - \log\frac{n}{n_0} - 1\right) + \frac{q(T_s)}{T_s}\right)dn + \tfrac{5}{2}nR\frac{dT_c}{T_c},$$

so

$$\frac{dT_c}{dn} = \frac{T_c}{n}\left(\tfrac{2}{5}(1 + \log\frac{n}{n_0}) - \log\frac{T_c}{T_0} - \tfrac{2}{5}\frac{q}{RT_s}\right).$$

Next

$$dW = \left(R(\tfrac{5}{2}T_c - \tfrac{7}{2}T_0) + q\right)dn + \tfrac{5}{2}nRdT_c,$$

so

$$\frac{dW}{dn} = R\left(\tfrac{7}{2}(T_c - T_0) + T_c(\log\frac{n}{n_0} - \tfrac{5}{2}\log\frac{T_c}{T_0})\right) - q(T_s)\left(\frac{T_c}{T_s} - 1\right). \tag{22}$$

4. Isothermal CAES

An alternative to the above adiabatic schemes is to do away with insulation and allow such good heat transfer between the environment and the cavern or airbag that it remains at constant temperature. For simplicity, take this to be the same as the temperature T_0 of the atmospheric air.

4.1. **Isothermal underwater airbag.** The work done in compressing n moles of an ideal gas isothermally from pressure P_0 to P_b is $W = nRT_0\log\frac{P_b}{P_0}$. This follows by integrating $\int P\,dV$ along the isotherm $PV = nRT_0$. Even if the compression is done by incrementally adding moles to the airbag, each mole of air gets its own volume in the airbag, so the result is the same. To this, one should add the work to displace water from the vicinity of the airbag to the surface but subtract off the work done by the atmosphere on the removed air and add the work done against the atmosphere in raising the water level, but for an isothermal ideal gas these cancel. Thus the stored exergy is

$$W = nRT_0\log\frac{P_b}{P_0},$$

and the volume in the airbag is

$$V = \frac{nRT_0}{P_b}.$$

Both are proportional to the number of moles stored. The coefficients of proportionality as functions of the pressure ratio are plotted in Figure 7.

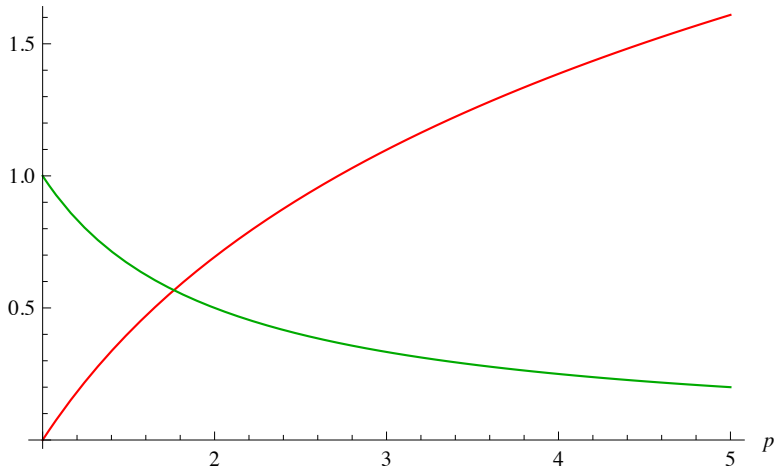

FIGURE 7. The stored exergy $w = W/n$ per mole (red) and volume $v = V/n$ per mole (green) relative to atmospheric volume, for an isothermal underwater airbag, as functions of the pressure ratio $p = \frac{P_b}{P_0}$.

Hence $\frac{W}{V} = P_b \log \frac{P_b}{P_0}$. This is compared with the adiabatic case (8) in Figure 8. Isothermal wins.

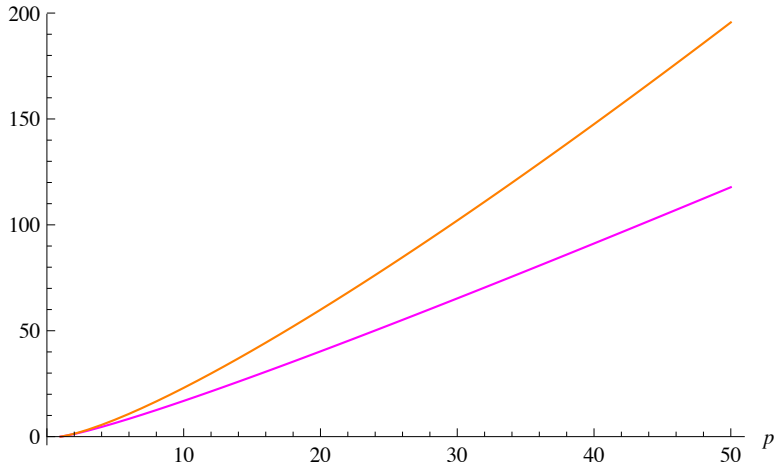

FIGURE 8. The ratio W/V for insulated (magenta) and isothermal (orange) underwater airbags, as functions of the pressure P_b in the bag, both scaled to P_0.

4.2. **Isothermal cavern.** The work to compress an extra δn moles into an isothermal cavern of volume V_c which started with $n_0 = \frac{P_0 V_c}{RT_0}$ moles at atmospheric conditions and now contains n moles is (to leading order in δn) $\delta n RT_0 \log \frac{n}{n_0}$, plus the work to compress the n moles by a factor $1 + \frac{\delta n}{n}$, minus the work done by the atmosphere in pushing the δn moles into the cavern. These last two contributions cancel, so we deduce that the stored exergy W satisfies

$$\frac{dW}{dn} = RT_0 \log \frac{n}{n_0}. \tag{23}$$

Integrating this with respect to n from n_0 we obtain

$$W = RT_0 \left(n \log \frac{n}{n_0} - n + n_0 \right). \tag{24}$$

The pressure in the cavern is simply $P = \frac{nRT_0}{V_c}$. These are plotted in Figure 9.

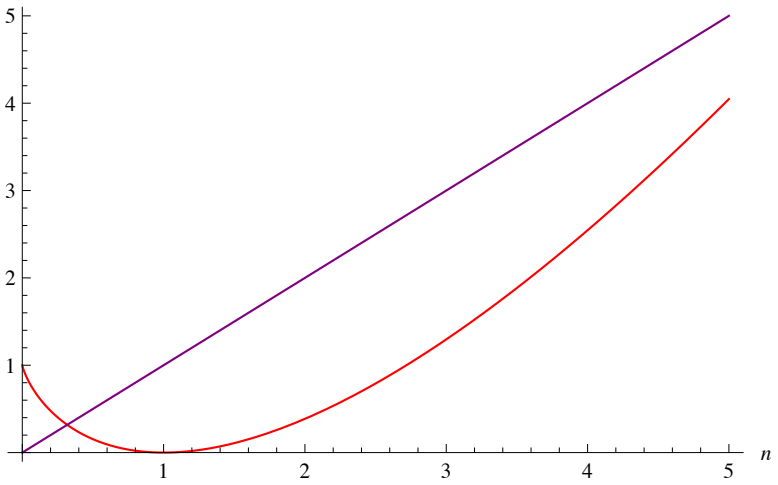

FIGURE 9. The stored exergy W (red) and pressure P (purple) for an isothermal cavern, as functions of the number n of moles in the cavern. The units are $P_0 V_c$, P_0 and n_0 respectively.

We compare W for isothermal (24) and adiabatic (6) caverns in Figure 10. Isothermal wins. Also, comparing with Figure 8, we see that underwater airbags win over caverns for the same pressure and volume.

5. Liquid-air energy storage

If one compresses and cools air enough then it liquifies. There is a large consequent reduction in volume, so the exergy density can be increased a lot as long as the associated heat stores do not take up too much space. Note that this is one place where it is especially clear we have to talk about exergy storage rather than energy, because the energy in liquid air is much less than in the corresponding atmospheric air but it is still useful as an exergy store. The idea of liquid-air energy storage (LAES) has been

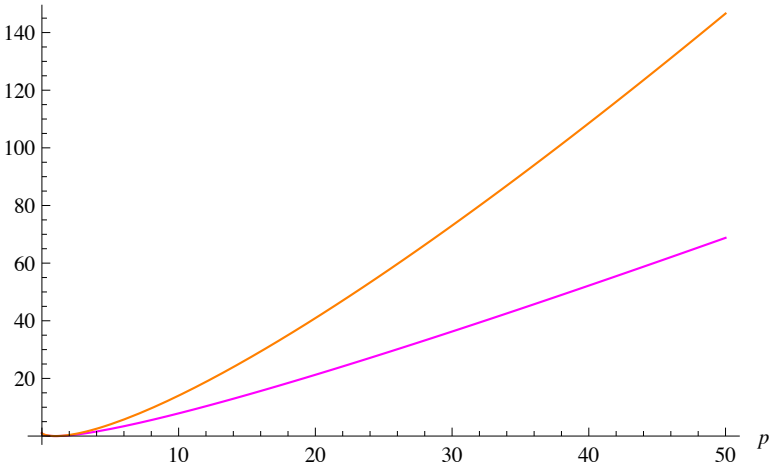

FIGURE 10. The stored exergy W for adiabatic (magenta) and isothermal (orange) caverns, as functions of the cavern pressure p. The units are P_0V_c and P_0.

explored by several groups, e.g. Ch.9 in [4], and a commercial facility is currently being built by Highview Power [15].

To treat the thermodynamics of liquefaction one has to abandon the realm of the ideal gas. Figure 11 from [16] shows a schematic entropy-temperature diagram for air. The top right corner B represents air at atmospheric conditions. The sloping curves are isobars. There is a curve through the points D and G, which bounds a region consisting of gas/liquid mixtures. To the right of this curve, the air is gas. To the left of the curve, the air is liquid. Above the curve it makes a continuous transition from gas to liquid. The maximum in the curve is the critical temperature of air, about 133K. It corresponds to a pressure of about 37 bar (approximately 3.7MPa).

If the goal is to reach the point D representing liquid air at atmospheric pressure at its boiling point (81K), then as argued in [16], the minimum work to achieve this is the area of the region ABGD, by compressing isothermally at atmospheric temperature to the point A and then expanding adiabatically to D. Taking atmospheric temperature of 290K, they calculated the stored exergy to be 0.19 kWh/kg (so 684 kJ/kg; [17] gives 739 kJ/kg but with atmospheric temperature of 300K). In practice, the pressure at A is too high, so one has to include an intermediate "cool" store. This increases the work required to liquefy 1kg of air, but from the view point of exergy storage, there is not necessarily any loss, the extra work simply going into exergy of the cool store. One can also include a heat store for the heat of compression instead of compressing isothermally.

A promising idea coming from a group in the IMAGES project is to combine CAES and LAES in series [18].

6. Refinements

There are many directions in which refinements to the above analyses are possible.

Most importantly, in practice, the processes are not reversible and this leads to exergy losses, corresponding to entropy increases. In particular, it is essential to make all heat

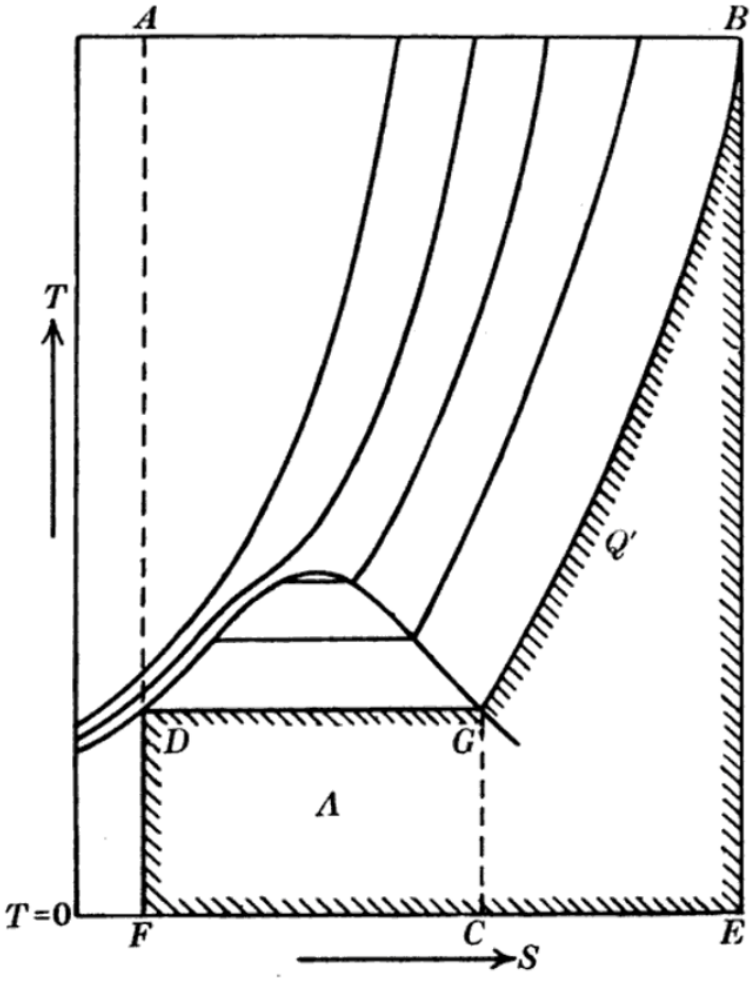

FIGURE 11. Schematic entropy-temperature diagram for air (fig.1 of Ch.II from [16]). Reproduced with permission of Cambridge University Press.

transfer between parts of the system be between equal temperatures (or as equal as possible). So there are losses if one compresses air to the outlet pressure but to a different temperature from the outlet side. Losses lead to reduced efficiency (energy out : energy in). For one study on efficiency, see [19], as well as the previously cited [18].

To make a substantial difference to world energy systems, it is essential for storage to achieve high efficiency. For this reason, insulated underwater airbag storage without heat store is promising: the pressure and temperature are independent of how full the bag is and they are related precisely by the law of adiabatic compression. For all the other adiabatic schemes and for the isothermal schemes one has to allow time for heat to flow in order not to build up temperature differences. Insulated underwater airbag storage without heat store also has the advantage that the compressor and expander

operate between fixed conditions (T_0, P_0) and (T_b, P_b) independent of how full the bag is, which makes their design and operation easier.

One could consider a precharged cavern, especially, as cavern pressure is usually not allowed to go below some P_{min} to avoid the risk of its collapsing. Then the outside air would in general be on the wrong adiabat, so some calculation like that with a heat store would be required.

For isothermal storage one could also consider the case where the store temperature is not atmospheric. For example, the temperature at the sea bed is around 4°C which is less than the typical atmospheric temperature. Then "isothermal" is a misnomer and in principle one could gain exergy continuously by pumping heat from the hotter to the cooler.

A variant of compressed air storage is being developed in Australia by Hydrostar, in which underground compressed air displaces water to a surface reservoir, combined with a heat store [20].

Moisture in the air leads to complications, both for modelling and in practice. Moisture leads to deviations from ideal gas behaviour and in expansion risks freezing into ice.

The IMAGES project looked also at purely thermal storage and at generation integrated energy storage (GIES). We have seen that much of CAES involves thermal storage; thermal storage on its own appears to be the most viable method for timescales of a day [2]. The idea of GIES is to colocate energy storage with generation and store some of the generated energy without first turning it into electricity [21]. For example, one could store some of the heat from nuclear reactions or burning coal as heat and turn it into electricity later, or one could use wind energy to compress air and turn it into electricity later.

Finally, the IMAGES project has developed an algorithm for optimal use of an energy store, either for arbitrage (making money from variations in price with time) or for smoothing (reducing the variation of the imbalance between supply and demand) [22]. It depends on predictions of future prices or imbalance, respectively, but only a finite time ahead (though for smoothing we do not yet incorporate rate constraints).

7. Conclusion

Following David's interest in sustainable energy, I have reviewed one strand, namely the thermodynamics of compressed air energy storage. There is a variety of schemes that could in principle operate at close to 100% efficiency. I have indicated that the relevant concept is exergy storage, being the work that can be done in relaxing the system to atmospheric temperature and pressure. One promising scheme is insulated underwater airbag storage, though isothermal would lead to higher exergy density if one could develop an efficient isothermal compressor/expander.

The idea of [18] to run compressed air and liquid air energy storage in series could be a promising example of a general principle. Living organisms store exergy in a hierarchy of densities and timescales, from charge separation of excitons in chloroplasts, $ATP \rightleftharpoons ADP + P_i$ disequilibrium, and proton motive force across membrane, to glucose, and starch/fat. Probably we need to design a hierarchy of types of energy storage operated in series according to their timescales and storage densities.

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